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PORTLAND HARBOR RI/FS  
FINAL NATURAL ATTENUATION TECHNICAL  
MEMORANDUM – SEDIMENTATION FIELD SAMPLING  
PLAN

September 2004

**Prepared for:**  
The Lower Willamette Group

**Prepared by:**  
Anchor Environmental, L.L.C.  
Texas A&M University



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## 1.0 INTRODUCTION

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This technical memorandum presents the Field Sampling Plan to collect information in support of the evaluation of natural attenuation processes for the Portland Harbor RI/FS. It has been prepared in accordance with the Portland Harbor RI/FS Programmatic Work Plan, specifically Appendix I, Attachment 4 of that document, "Natural Attenuation Data Gaps Technical Memorandum". The RI/FS Programmatic Work Plan (Work Plan) describes a three step process for evaluating natural attenuation processes at the Portland Harbor site:

Step 1 - Identify areas that have basic processes that are potentially suitable for natural attenuation based on general information about the river system.

Step 2 - Conduct select sampling (in Round 2) within a few areas that appear characteristic of the range of potential natural attenuation processes at the Site and conduct simple probabilistic modeling. Eliminate from future evaluations the types of areas that have a low probability of having processes that support natural attenuation.

Step 3 - Conduct detailed sampling (in Round 3) and modeling in Sediment Management Areas (SMAs) that appear to have suitable processes for natural attenuation (based on Step 2 results) to determine viability and rate of natural attenuation.

This technical memorandum presents the Field Sampling Plan (FSP) for the select sampling in Step 2 including detailed sampling and analysis procedures. The data evaluation methods for Step 2 using the data collected per this FSP will be described in a follow up Technical Memorandum that will be submitted to EPA for review.

Although this FSP describes collection of information that focuses on processes (e.g., bioturbation, sediment dynamics, and sedimentation) that can be particularly important "drivers" of natural attenuation in many situations, this does not mean that other processes such as diffusive and advective dissolved transport of chemicals are ignored by the overall evaluation methodology. All of the natural attenuation processes discussed in the Work Plan will be evaluated in detail, as needed, at some point in the evaluation process. This overall evaluation process is described in detail in the Work Plan.

## **2.0 ROUND 2 SEDIMENT CORE SAMPLING LOCATIONS**

---

This section presents the sediment core sampling locations. The major data gaps identified in the Work Plan for Step 2 modeling are:

- Collection of subsurface sediment cores for sampling of radioisotope profiles
- Collection of water column samples for chemical analysis and determination of total suspended solids content.

These data represent the most critical information to further understanding whether and where natural attenuation processes occur at the site. This conclusion is based on the evaluation and modeling framework developed in the Work Plan.

Most of this document focuses on the subsurface coring and radioisotope sampling of those cores, while water column sampling is discussed further in Section 4.4. In summary, the water column sampling described in the Portland Harbor RI/FS Draft Round 2 Surface Water FSP (Integral 2004) will provide information for natural attenuation evaluation, and description of those sampling and analysis procedures are not duplicated here.

Subsurface coring for radioisotope analyses provides a means to date the stratigraphy of the sediments. That is, the time at which each layer of sediments was deposited can be determined from this technique. The cores are sectioned into relatively small slices each of which is submitted for dating analysis. Once the approximate age of each layer is known, this information can be used to estimate the depth and rate of any bioturbation activities in the surface sediment layers as well as the long term sedimentation rates indicated by subsurface layers in that area. The vertical profile of radioisotopes can also provide valuable information on the stability and/or periodic erosion of the sediment bed. The bioturbation characteristics and sedimentation rates are key input parameters for virtually any kind of natural attenuation estimates or models that might be used for this project.

The goal of the subsurface sediment sampling is to select a few areas for sampling that will provide information on the presence, general character, and rates of these processes at some potential key locations. This information will be used in Step 2 of the natural attenuation evaluation process and will be use to evaluate the need for further and more specific data collection in Round 3.

Consequently, four sampling sites for subsurface cores were chosen at key locations that appear to have the potential general physical characteristics of a sedimentation type environment (Figure 1). The specific rationale following the above general approach for each sampling site is detailed in the following subsections. The proposed locations are shown in Figures 1.

## **2.1 CORE NA-1**

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This core is located near Linnton Plywood (Figure 1). This location was chosen because it appears typical of nearshore conditions on this side of the river. The station location is set outside of the extreme shallows in this area so that it is approximately midway between areas that may be subject to wave erosion and deeper areas that may be periodically dredged.

## **2.2 CORE NA-2**

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This core is located in Willamette Cove (Figure 1). The station is set some distance away from the shoreline for the same reasons as noted for Core NA-1.

## **2.3 CORE NA-3**

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This core is located at Willbridge Terminal (Figure 1). The station is set away from recent dredge areas and in an area where recent shallowing has been measured. The station is set approximately midway between the shoreline and the river-ward edge for the same reasons discussed above.

## **2.4 CORE NA-4**

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This core is located in the Portland Shipyard (Figure 1). The core location is toward the center of the waterway, away from potentially disturbing influences of propwash at the nearshore docks and dredge areas associated with the Cascade General operations. However, it should be noted that propwash and ship scour effects probably occur throughout this active waterway and cannot be totally avoided by any sample location.

## **2.5 AREAS NOT SPECIFICALLY SAMPLED**

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Collection of four subsurface cores provides information on a portion of the entire set of physical conditions in this region of the river. Preliminary results of the hydrodynamic modeling, when available, may help to understand how the physical conditions in the areas sampled relate to other areas of the site. In some cases, it may be possible to make estimated extrapolations to a range of reasonable sedimentation and bioturbation rates for other areas. At a minimum, the range of conditions in nearshore areas sampled can be applied to other areas to determine the extent to which natural attenuation may even be possible. If such preliminary extrapolations indicate some potential for natural attenuation, additional site specific samples could be collected in a larger number and greater variety of locations in Round 3.

### **3.0 FIELD SAMPLING PROCEDURES**

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Subsurface radioisotope cores will be collected at the stations described in the previous section. This section describes the FSP procedures for these cores and includes detailed procedures for sampling, processing, and analysis of the core samples. The natural attenuation coring will be conducted using coring equipment and procedures identical to those described for the much larger Round 2 sediment sampling event that is described in the Portland Harbor RI/FS Round 2 FSP for Sediment and Benthic Toxicity Testing (hereafter referred to as the Round 2 Sediment FSP; Integral et al. 2004). Consequently, many of the detailed procedures discussed in the Round 2 Sediment FSP and associated Round 2 QAPP (Integral and Windward 2004) are incorporated here by reference.

#### **3.1 ORGANIZATIONS AND RESPONSIBILITIES**

---

Overall management of the natural attenuation sampling and analysis will be by Anchor Environmental, L.L.C (Anchor). On-water field activities will be directed by Integral Consulting, Inc. (Integral) including mobilization of coring field equipment, supplies, and coring contractors; and collection of sediment cores. Integral will also be responsible for assuring accurate station positioning; accurately labeling each core; proper decontamination procedures for coring equipment; and recording sample locations, depths, and coordinates. Per the Round 2 Sediment FSP, specific personnel from Integral include: Keith Pine for CERCLA Project Coordinator and Gene Revelas for Sampling and Analysis Coordinator. Specific personnel from Anchor Environmental include Carl Stivers as the Sampling and Analysis Coordinator and James Keithly for the Field Coordinator for radioisotope core processing, sampling, and analysis.

The cores (in intact sections) will be provided to Anchor for onshore processing (e.g., splitting and subsampling of cores), and delivery of samples to the laboratories. Anchor will assure conformance to sampling and handling requirements including field decontamination procedures for sampling equipment; logging and physical evaluation of the cores and samples; and completing Chain-of-Custody (COC) forms, as is specified in the Round 2 Sediment FSP, the Round 2 QAPP, and the laboratory QAPP for these radioisotope analyses (Attachment 1). Anchor will also coordinate with the laboratories as necessary to ensure that all samples are analyzed consistent with this FSP and the two QAPPs.

Laboratory bulk metals, organic chemistry, and conventional (e.g., total organic carbon, grain size) analyses of sediment samples will be conducted by a certified laboratory chosen for these analyses for the overall Round 2 sediment sampling event and are identified in the Round 2 Sediment FSP and Round 2 QAPP. Radioisotope sediment analyses will be conducted by Texas A&M University Laboratory for Oceanographic and Environmental Research (LOER).

All other responsibilities and procedures will be consistent with the Round 2 Sediment FSP.

### **3.2 SUBSURFACE CORE SAMPLE COLLECTION**

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Sample collection will follow the procedures described in the Round 2 Sediment FSP including specifics relating to:

- sampling vessels used
- station positioning and vertical control
- field logbooks and forms
- equipment and supplies
- equipment decontamination procedures
- field quality assurance/quality control procedures (where applicable to natural attenuation coring)
- subsurface sediment core collection procedures
- waste disposal
- sample handling and transport.

At each sampling location depicted in Figure 1, two cores will be taken. These cores will be taken as close together as possible, while ensuring that the sediments disturbed by one core are not sampled by the second core. A target distance for this purpose will be 1 to 2 ft from the previous core location. The first core will always be subjected to radioisotope analyses, and is termed the “radioisotope core”. The second core will be sampled for ancillary information on sediment bulk chemistry and physical characteristics, and is termed the “ancillary core”.

Natural attenuation subsurface radioisotope and ancillary cores will be penetrated to a depth of 4 m (400 cm or approximately 13 ft) or refusal, whichever is less. Acceptance criteria for these cores will be the same as for other subsurface coring described in the Round 2 Sediment FSP.

#### **3.2.1 Radioisotope Core Processing**

Radioisotope core processing will begin by cutting the core at 94 cm (3.1 ft) (consistent with the sampling approach shown in Figure 2) from the top of the mudline in the core and capping the bottom portion of the core. The bottom portion (below 94 cm) will be archived intact and may be cut into additional sections for easy handling as needed (with proper labeling of each section for later identification).

The core above 94 cm (upper portion) will be cut open longitudinally. Physical descriptions of the core will be noted on a core profile form. One half of the split core will be sampled for  $^7\text{Be}/^{137}\text{Cs}$  analyses and the other half for  $^{210}\text{Pb}$ /bulk metals analyses. Samples submitted for  $^7\text{Be}/^{137}\text{Cs}$  analyses will be obtained by the



laboratory from the same sample jar. Samples for  $^{210}\text{Pb}$ /bulk metals analyses will be homogenized and then split equally between two jars, one for  $^{210}\text{Pb}$  analysis by LOER and one for bulk metals analysis at the standard laboratory.

Samples will be taken at the core intervals shown in Figure 2. These are fixed intervals and will be sampled regardless of changes in sediment type. As shown in Figure 2, this sampling scheme will result in 18 samples for  $^7\text{Be}/^{137}\text{Cs}$  analysis and 15 samples for  $^{210}\text{Pb}$ /bulk metals analysis. Intervals not sampled in the upper portion of the core will be placed in jars and archived as shown in Figure 2.

### **3.2.2 Ancillary Core Processing**

Ancillary core processing will begin by cutting the core at 94 cm (3.1 ft) from the top of the mudline in the core and capping the bottom portion of the core. The bottom portion (below 94 cm) will be archived intact and may be cut into additional sections for easy handling as needed (with proper labeling of each section for later identification).

The core above 94 cm (upper portion) will be cut open longitudinally. Physical descriptions of the core will be noted on a core profile form and compared to the core profile noted for the radioisotope core. Major vertical changes in physical characteristics or “strata” will be noted. Major strata will be sampled (up to 3 samples per core) for bulk organic chemistry and conventional analyses. Volatile organic chemical sampling will proceed first, and will follow the procedures in the Round 2 Sediment FSP including no homogenization and placement of sampled sediments directly into jars. Prior to sampling of strata for remaining laboratory analytes, pH and Eh will be measured in each strata and immediately on either side of any visually apparent surface redox boundary using field probes. Each strata to be sampled will then be removed and homogenized in a bowl. Once the sample is homogenized, jars for other organic chemical and conventional sediment analyses will be filled. Bulk sediment chemistry and conventional sample collection and analysis will follow the procedures in the Round 2 Sediment FSP. Samples for these analyses will be submitted to the laboratories designated in the Round 2 Sediment FSP for analyses using the methods described in that same document.

### **3.2.3 Sample Location Identification Scheme**

Each sample station will be assigned a unique alpha-numeric identifier. Sediment samples will be recorded according to the method described below. The identifiers facilitate sample tracking by incorporating identifying information. The alpha-numeric identifiers will be assigned as follows:

- The first two characters identify the sample type with “NA” indicating Natural Attenuation samples.

- The third character identifies the sample station location with each station numbered 1 – 4 as shown in Figure 1
- The fourth character identified the whether the sample came from the first (“A”) or second (“B”) core at that station.
- The subsequent characters identify the core sample interval in cm: 1620 = core sample interval from 16 to 20 cm.

For example, sample number NA-1A-1620 indicates a sediment sample for the station near Linnton Plywood obtained from 16 to 20 cm in depth in that core. In addition, each jar filled from that sample will be identified with the analysis required from that jar.

### **3.3 SAMPLE CONTAINERS, PRESERVATION, AND HOLDING TIMES**

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Sample containers, preservation requirements, and holding times for radioisotope analyses are shown in Table 1. The requirements for all other analysis types will be consistent with Table 4-1 of the Round 2 Sediment FSP.

### **3.4 PHYSICAL AND CHEMICAL ANALYSES**

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This section summarizes the physical and chemical analyses performed for the characterization of sediment samples. The proposed analytes for radioisotope cores are:

- $^7\text{Be}$  by gamma counting as described in the laboratory QAPP (Attachment 1)
- $^{137}\text{Cs}$  by gamma counting (Attachment 1)
- $^{210}\text{Pb}$  by alpha counting (Attachment 1)
- Total solids (Attachment 1)
- Bulk sediment metals using methods described in the Round 2 Sediment FSP (Table 4-1)
  - Arsenic
  - Cadmium
  - Chromium
  - Copper
  - Lead
  - Nickel
  - Silver
  - Zinc

Attachment 1 presents the proposed analytical methods for radioisotope determinations and total solids determinations. Bulk metals analytical methods and

detection limits are described in the Round 2 Sediment FSP and Round 2 QAPP. Total solids will be separately determined by the bulk metals laboratory using methods in the Round 2 Sediment FSP for comparative purposes.

The proposed chemical/physical analyses for samples from the ancillary cores will include:

- Semi-volatile organic compounds (SVOCs)
- PCB Aroclors
- Chlorinated pesticides
- Volatile organic compounds (VOCs).
- Total Petroleum Hydrocarbons (TPH) – gasoline, diesel, and oil ranges
- Grain size
- Total organic carbon
- Specific gravity
- Water content/total solids

The chemical parameter list for each chemical category, chemical and physical analytical methods, and detection limits for each parameter will follow the requirements of the Round 2 Sediment FSP and Round 2 QAPP. Analyses will be conducted by those laboratories designated in Table 4-1 of the Round 2 Sediment FSP.

### **3.5 WATER COLUMN SAMPLING AND ANALYSIS PROCEDURES**

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Water column sampling and analysis procedures are described in the Round 2 Surface Water FSP. The information obtained from this sampling event will be used for a number of purposes including filling natural attenuation data gaps for Step 2 of the natural attenuation evaluation process. Water column samples will be collected at numerous locations throughout the ISA as specified in the Round 2 Surface Water FSP and analyzed for a full suite of chemical analytes as well as Total Suspended Solids (TSS). This information will be used to estimate the concentrations of chemicals in settling sediments at various locations throughout the ISA. For this purpose, the focus will be on near-bottom samples, but all samples obtained for the Round 2 Surface Water FSP will be evaluated for potential use in the Step 2 natural attenuation evaluation and modeling. Analyte detection limits described in the Round 2 Surface Water FSP will be adequate for the preliminary assessment proposed for Step 2. In general, TSS detection limits should be at (or, where possible below) 1 mg/L as specified in the Round 2 Surface Water FSP.

The surface water data will be used to calculate the concentration of chemicals potentially present in and on suspended sediment particles in the water. This concentration will then be used as an estimate of chemical concentrations in particulates that might settle out of the water column and onto the sediment bed over

time. For this calculation, the dissolved fraction of the chemical in water will be subtracted from the total fraction of the chemical in water to obtain a chemical concentration associated with particulates. Where only total concentrations of a chemical are measured, it will be assumed that the entire concentration represented by that value is present in particulate form. This latter assumption tends to over predict the concentrations of chemicals in the particulate phase, but is conservative for the purposes of predicting natural attenuation (tends to underestimate any natural attenuation rates). The concentration of a chemical in suspended sediments is obtained by multiplying the water concentration in mg/L divided by the suspended sediments concentration in kg/L to obtain a chemical particulate concentration in mg/kg.

## 4.0 REFERENCES

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Integral Consulting, Inc. 2004. Portland Harbor RI/FS Round 2A Field Sampling Plan Surface Water Sampling Draft. Prepared for Lower Willamette Group. Seattle, Washington.

Integral Consulting, Inc., Anchor Environmental, L.L.C., and Windward Environmental L.L.C. 2004. Portland Harbor RI/FS Round 2 Field Sampling Plan Sediment Sampling and Benthic Toxicity Testing. Prepared for Lower Willamette Group. Seattle, Washington.

Integral Consulting, Inc. and Windward Environmental, L.L.C. 2004. Portland Harbor RI/FS Round 2 Quality Assurance Project Plan. Prepared for the Lower Willamette Group. Seattle, Washington.

**Table 1. Sample Containers, Holding Times, and Preservation Requirements.**

| Parameter   | Container Size and Type | Holding Time | Preservative |
|---|-------------------------|--------------|--------------|
| <b>Sediment Core Samples</b>                      |                         |              |              |
| <sup>210</sup> Pb, water content                  | 150 ml HDPE             | 6 months     | Cool/ 4°C    |
| <sup>7</sup> Be/ <sup>137</sup> Cs, water content | 150 ml HDPE             | 90 days      | Cool/ 4°C    |
|   |                         |              |              |



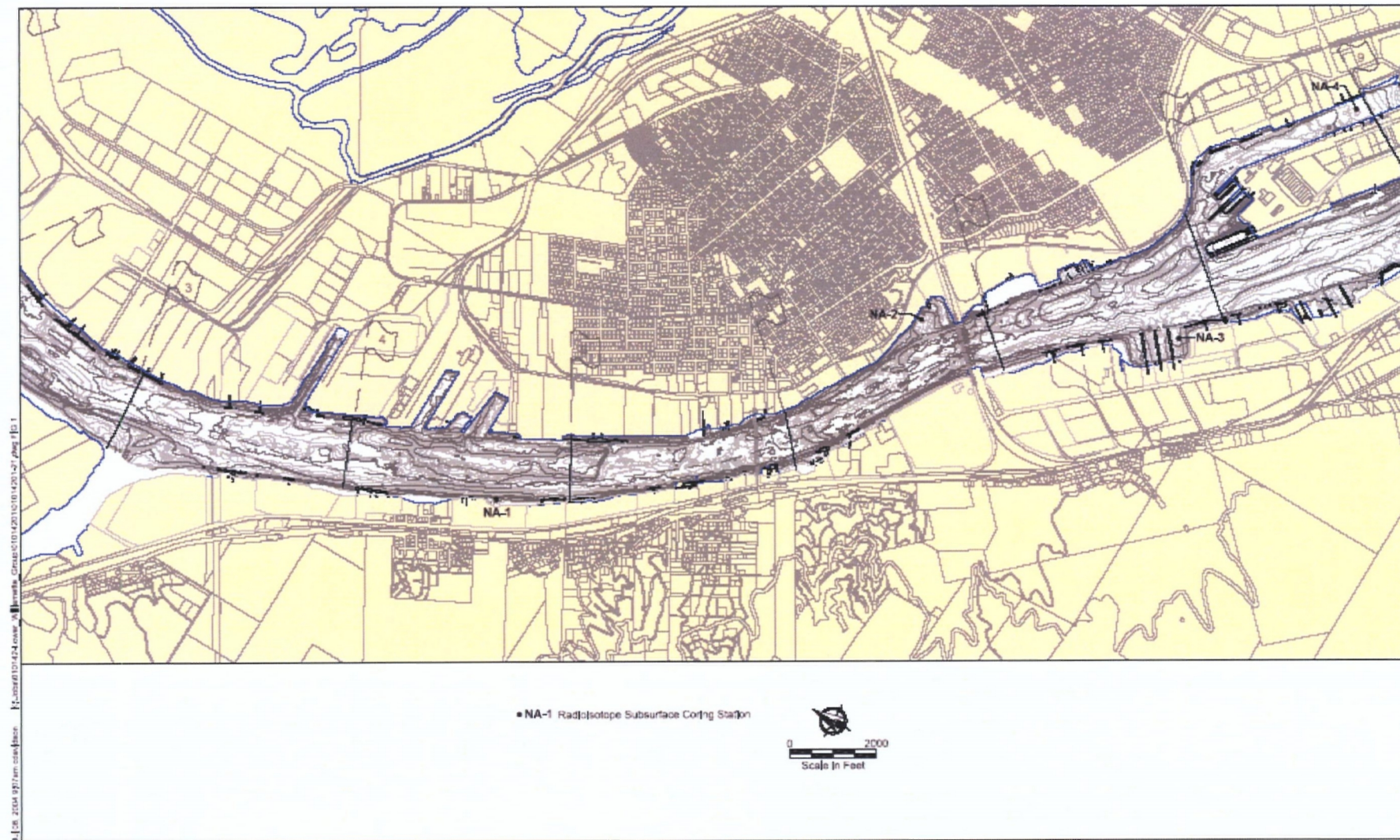


Figure 2. Natural Attenuation Core Sampling Schematic.

| Sample Depth (cm) |        | <sup>7</sup> Be/<br><sup>137</sup> Cs | <sup>210</sup> Pb/<br>Metals |
|-------------------|--------|---------------------------------------|------------------------------|
| top               | bottom |                                       |                              |
| 0                 | 0.5    | 1                                     | 1                            |
| 0.5               | 1      | 1                                     |                              |
| 1                 | 1.5    | 1                                     |                              |
| 1.5               | 2      | 1                                     |                              |
| 2                 | 3      | 1                                     |                              |
| 3                 | 4      | 1                                     |                              |
| 4                 | 5      | 1                                     |                              |
| 5                 | 6      | 1                                     | 1                            |
| 6                 | 7      | 1                                     |                              |
| 7                 | 8      | 1                                     |                              |
| 8                 | 9      | 1                                     | 1                            |
| 9                 | 10     | 1                                     |                              |
| 10                | 12     | 1                                     |                              |
| 12                | 14     |                                       |                              |
| 14                | 16     | 1                                     | 1                            |
| 16                | 18     |                                       |                              |
| 18                | 20     | 1                                     | 1                            |
| 20                | 22     |                                       |                              |
| 22                | 24     | 1                                     | 1                            |
| 24                | 26     |                                       |                              |
| 26                | 28     | 1                                     | 1                            |
| 28                | 30     |                                       |                              |
| 30                | 32     | 1                                     | 1                            |
| 32                | 34     |                                       |                              |
| 34                | 36     | Archive                               | 1                            |
| 36                | 38     |                                       |                              |
| 38                | 40     |                                       |                              |
| 40                | 42     | Archive                               | 1                            |
| 42                | 44     |                                       |                              |
| 44                | 46     |                                       |                              |
| 46                | 48     | Archive                               | Archive                      |
| 48                | 50     |                                       |                              |
| 50                | 52     | Archive                               | 1                            |
| 52                | 54     |                                       |                              |
| 54                | 56     |                                       |                              |
| 56                | 58     | Archive                               | Archive                      |
| 58                | 60     |                                       |                              |
| 60                | 62     | Archive                               | 1                            |
| 62                | 64     |                                       |                              |
| 64                | 66     |                                       |                              |
| 66                | 68     | Archive                               | Archive                      |
| 68                | 70     |                                       |                              |
| 70                | 72     |                                       | 1                            |
| 72                | 74     | Archive                               |                              |
| 74                | 76     |                                       |                              |
| 76                | 78     |                                       | Archive                      |
| 78                | 80     | Archive                               |                              |
| 80                | 82     |                                       | 1                            |
| 82                | 84     |                                       |                              |
| 84                | 86     | Archive                               |                              |
| 86                | 88     |                                       | Archive                      |
| 88                | 90     |                                       |                              |
| 90                | 92     | Archive                               | 1                            |
| 92                | 94     |                                       |                              |
| 94                | 440    | Archive                               | Archive                      |

1 the depths within each box  
will be composited to make  
one sample



## **ATTACHMENT 1**

### **LABORATORY QUALITY ASSURANCE PROJECT PLAN**

|                                 |  |
|---------------------------------|--|
| <b>PROJECT TITLE:</b>           | <b>Radiochemical Studies</b>   |
| <b>DATE PREPARED:</b>           | <b>July 14, 2004</b>   |
| <b>PREPARED BY:</b>             | <b>Peter H. Santschi, Galveston, TX 77551</b>  |
| <b>PROJECT TYPE:</b>            | <b>Extramural</b>  |
| <b>PERFORMING ORGANIZATION:</b> | <b>Peter H. Santschi, consultant.</b>  |
| <b>FACILITIES:</b>              | <b>Laboratory for Oceanographic and<br/>Environmental Research (LOER),<br/>of the Texas A&amp;M University at<br/>Galveston (TAMUG), Ft. Crockett<br/>Campus, 5007 Ave U, Galveston,<br/>TX 77551.</b> |
| <b>PROJECT MANAGER:</b>         | <b>Peter H. Santschi</b>   |

## PROJECT ORGANIZATION AND RESPONSIBILITY

| <u>PERSONNEL</u>                  | <u>AFFILIATION</u> | <u>PROJECT RESPONSIBILITY</u>  |
|-----------------------------------|--------------------|--|
| Peter H. Santschi                 | TAMUG              | Principal Investigator and Quality Assurance Officer. Will oversee and participate in data analysis and final data report. |
| Kevin Yeager and<br>Kathy Schwehr | TAMUG              | Radiochemistry Analysts. Will conduct sample handling and will be responsible for sample custody.                          |

## SUMMARY

This study will provide radiochemical data for Portland Harbor.

## PROJECT SCOPE

The data obtained in this research study will aid in the interpretation of chemical data on contaminants distribution.

## QUALITY ASSURANCE OBJECTIVES

1. To assure that data acquisition, transfers, and data analysis are carried out according to protocol.
2. To make sure that laboratory SOPs are followed and that any changes to them are recorded.
3. To maintain ongoing problem logs.

## SAMPLING PROCEDURES

Quality assurance factors related to the collection of sediments for radiochemical analysis of sediment samples includes the prevention of cross-contamination between samples, and the proper logging and description of all samples

### Minimization of background contamination

For radiochemical analysis, concentrations which are close to natural ones are measured. Therefore, contamination control is assured through normal laboratory procedures.

### Sample collection

Sediment collection will be handled by Anchor Environmental.

## SAMPLE CUSTODY AND HANDLING PROCEDURES

Sediment samples are shipped to the Texas A&M laboratory in Galveston, Texas in a cooler by an Express Mail carrier such as Federal Express, and stored in a lockable refrigerator located in Room 100 of Ft. Crockett, TAMUG, until further processing. A notebook is kept for each analytical procedure that coincides with all the checklists. From the day the samples are collected, until the day the samples are analyzed, everything is recorded in laboratory check lists and note books, and both are saved in a lockable cabinet (safe) located in Room 200 Ft. Crockett, TAMUG, when not in use. Keys to this cabinet are kept by Drs. Kevin Yeager and Kathy Schwehr, postdoctoral research associates, and Dr. Peter H. Santschi.

After the samples have all been analyzed, the results are input into spreadsheets by each analyst.

In the laboratory, core material is handled for radiochemical and porosity analysis by Drs. Kevin Yeager and Kathy Schwehr, postdoctoral research associates.

*a) Processing of sediment samples.*

Sediment samples from core material sent to us are handled by Drs. Kevin Yeager and Kathy Schwehr. Each sample used for analysis is homogenized if wet. About 2 g of wet sediment is taken for drying, while the rest of each sample is oven dried for 24h at 80 °C, after weighing each wet sediment sample. Samples are then re-weighted when dry, and dried samples are homogenized through pulverization (SPEX 8000 mixer/mill).

Subsamples of the oven dried sediments are taken and weighed for the following radiochemical analyses at the LOER lab at Galveston.

- About 1 g dry sediment 210Pb analysis by wet chemistry and alpha counting.
- About 10g dry sediment for gamma counting, and subsequent wet chemistry followed by alpha counting for 210Pb at the LOER lab in Galveston.

## **ANALYTICAL PROCEDURES**

Details of the analytical procedures are given in Appendix I

### **CALIBRATION PROCEDURES AND FREQUENCY**

For each analytical procedure, precision and accuracy are determined through replicates (10%) and analysis of standard reference materials, as described in Appendix I.

### **DATA REDUCTION, VALIDATION AND REPORTING**

Data reduction and validation will be carried out separately by Drs. Kevin Yeager and Kathy Schwehr (radiochemistry and porosity).

### **INTERNAL QUALITY CONTROL CHECKS**

Refer to Appendix I for internal quality control.

### **PERFORMANCE AND SYSTEM AUDITS**

Dr. Peter H. Santschi will obtain bi-weekly progress reports by each subprogram investigator and will review all data obtained so far. Gamma and Alpha Counting equipment maintenance and equipment performance audits will be carried out by Drs. Kevin Yeager and Kathy Schwehr.

## **PREVENTATIVE MAINTENANCE**

Prior to initiating the study, all instrumentation for conducting the experimental work will be reviewed and appropriate repairs will have been made.

## **DATA PRECISION, ACCURACY AND COMPLETENESS**

For each subprogram, appropriate replicates (~10% of samples) and standards, as described in Appendix I, will be analyzed during the study. If the results are suspect, new material will be reanalyzed. Typical data precision and accuracy for each method are given in Appendix I.

## **CORRECTIVE ACTION**

Monthly meetings will be held to discuss any potential problems, and their resolutions will be documented in Memos.

## **QUALITY ASSURANCE REPORTS**

At the end of the study, a final summary QA report which will include all data calibrations and standardizations, to be included with the data report, prepared by Dr. Peter H. Santschi.

## APPENDIX I.

### Detailed Analytical Procedures for Radiochemistry Program.

#### 1) Overview of Radiochemical Procedures

The radiochemical program can include the following isotopes.

$^{239,240}\text{Pu}$ : Samples of about 10 g each, by alpha counting, after chemical separation, according to procedures described in Santschi et al. (1980), Baskaran et al. (1995) and Ravichandran et al. (1995a).

$^{210}\text{Pb}$ : Samples of 1 g each by alpha counting, after complete digestion and chemical separation, according procedures given in Santschi et al. (1980), Ravichandran et al. (1995b), and Santschi et al. (1999). Gamma counted samples will result in another, but often less precise,  $^{210}\text{Pb}$  value, to be used for comparison purposes. It is expected that excess- $^{210}\text{Pb}$  activity (i.e., [ $^{210}\text{Pb}$ ] -  $^{226}\text{Ra}$ ) will be detectable in more than 50% of the sediment samples.

$^{226}\text{Ra}$ : Samples of 10 g each by non-destructive gamma counting, according to procedures given in Santschi et al. (1980), Baskaran et al. (1995), Ravichandran et al. (1995b), and Santschi et al., (1999).

$^{234}\text{Th}$ : Samples of 10 g each by non-destructive gamma counting, according to procedures given in Santschi et al. (1980, 1999). It is expected that only the top 10 cm of sediments will show measurable excess- $^{234}\text{Th}$  activity (i.e., [ $^{234}\text{Th}$ ] - [ $^{238}\text{U}$ ]), but results will be available for all samples, down to about 50 cm.

$^{137}\text{Cs}$ : Samples of 10 g each by non-destructive gamma counting, according to procedures given in Wan et al. (1986), Schuler et al. (1991), and Santschi et al. (1999).

$^7\text{Be}$ : Samples of 10 g each by non-destructive gamma counting, according to procedures given in Wan et al. (1986), Schuler et al. (1991) and Santschi et al. (1999).

References can be found in the Appendix II.

#### 1.1) Details of analytical steps.

Sediment samples of about 10g size will be used for non-destructive gamma counting in a low-background, high-efficiency high-purity Germanium (HPGe) well detector, followed by wet chemical extraction procedures and alpha counting (or AMS) for individual radionuclides. All 50 samples will thus first be gamma counted and then processed for wet chemical/alpha counting analyses for Pu and Pb isotopes.

The sequence of steps to be followed is as follows:

- gamma counting of samples for 1 day to obtain results for  $^{210}\text{Pb}$  (46 keV),  $^{234}\text{Th}$  (63 keV),  $^{226}\text{Ra}$  (352 keV),  $^7\text{Be}$  (478 keV),  $^{137}\text{Cs}$  (662 keV),
- $^{210}\text{Pb}$  analysis by wet chemistry followed by alpha counting for 1-2 days,
- $^{239,240}\text{Pu}$  analysis by wet chemistry (8 days) followed by alpha counting for 1-2 days.

The check list for the Pb and Pu procedures is attached in the appendix. The general procedures to be followed are listed in appendix I.

Separately freeze dried sediment samples will be screened under the microscope for organic fragments, to be sent off for  $^{14}\text{C}$  analysis at the Accelerator Mass Spectrometry Center of the Woods Hole Oceanographic Institution. Results will be reported as  $\Delta^{14}\text{C}$  and apparent age.

## **2) Chemical extraction and separation procedures.**

### **2.1.1) Sample Pre-treatments for Alpha Counting of $^{210}\text{Pb}$**

#### *2.1.1.1) Sample Total Dissolution:*

1. Weigh out dried sediment (0.5 – 1.5g) and record weight. Add to small amount of distilled water in a 100 or 250ml Teflon beaker.
2. Add appropriate tracer, in this case  $^{209}\text{Po}$  (0.5 ml @ 9.60 dpm/ml).
3. Add 10 – 15ml each of concentrated HCl,  $\text{HNO}_3$  and HF to sample and heat at  $\approx 3$  on hotplate until dissolution/evaporation is nearly complete (near dryness).
4. Repeat step 3.
5. Add 10 – 15ml each of concentrated HCl and  $\text{HNO}_3$  and repeat heating and evaporation (near dryness) process.
6. Repeat step 5 (if refractory minerals are still present after this step, begin again at step 3 (very rare)).
7. Add 20 – 30ml of concentrated HCl and heat to near dryness.
8. Bring up in 50ml of 1.5N HCl for Po plating.

#### *2.1.1.2) Polonium Separation and Plating:*

1. Transfer #8 above to a 100ml Teflon beaker and add a small stir bar.
2. Heat and stir at  $\approx 2$  (big hotplate (BH)) or 3 (little hotplate (LH)) for 15 minutes.
3. Add ascorbic acid and stir vigorously to dissolve, repeat until all Fe is complexed (remove most of the yellow coloring, 2-3 small spatulas is all that is ever required).
4. Heat and stir for another 15 minutes, then check color, if yellow persists (rare), add more ascorbic acid, otherwise proceed.
5. Add prepared Ag disc to sample solution (Ag disc needs taped, cut, polished, rinsed w/ DI, plated & labeled).
6. Heat (2 (BH) 3 (LH)) and stir gently for 2.5 hours. Check periodically for discoloration due to Fe oxidation (if so, then add more ascorbic acid to remove color (again, rare)).

7. Remove disc from sample solution, wash with water and acetone, label and store for counting. Properly dispose of solution.

### 3) Alpha counting procedures

#### 3.1) $^{210}\text{Pb}$

$^{210}\text{Po}$  and  $^{239,240}\text{Pu}$  are assayed separately on alpha counters. The Canberra's *Quad Alpha Spectrometer* with ultra-low background surface barrier detectors are used for this purpose. These detectors have an active area of 450 mm<sup>2</sup> and an alpha resolution of 20 keV. The detectors are coupled to a S100 Canberra Multi-Channel Analyzer. The background counts of these detectors are typically about 1-2 counts per day in the regions of interest.

Secular equilibrium between  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  is assumed to exist before alpha counting for  $^{210}\text{Po}$ . A known amount of  $^{208}\text{Po}$  spike was added to the sediment samples before digestion. The energies of alpha particles emitted by  $^{210}\text{Po}$  is 5.30 MeV and by  $^{208}\text{Po}$  is 5.11 MeV (LEDERER and SHIRLEY, 1978). The activity of  $^{210}\text{Po}$  (dpm g<sup>-1</sup>) in the sediment samples was calculated using the formula:

$$^{210}\text{Po Activity (dpm/g)} = \frac{^{210}\text{Po counts (net)}}{^{208}\text{Po counts (net)}} \times \frac{^{208}\text{Po activity added (dpm)}}{\text{Wt. of sample (g)}} \times e^{\lambda t}$$

where,  $\lambda$  = decay constant of  $^{210}\text{Po}$  (= 0.693 / 138 days);  $t$  = the time between plating and mid-time of counting (in days). The  $^{208}\text{Po}$  spike has a relatively short half-life of about 2.8976 years and therefore, it was always decay corrected for the time since it was actually prepared. This was done using the formula:

$^{208}\text{Po activity at the time of use (dpm)} = ^{208}\text{Po activity when it was prepared (dpm/ml)} \times \text{vol. of spike (ml)} \times e^{-\lambda t}$  where,  $\lambda$  = decay constant of Po-208 (= 0.239 y<sup>-1</sup>);  $t$  = time between mid-counting and the time since preparation (in years).

#### 3.2) $^{239,240}\text{Pu}$

$^{239}\text{Pu}$  and  $^{240}\text{Pu}$  are the dominant isotopes from fallout plutonium.  $^{239}\text{Pu}$  has a half life of  $2.41 \times 10^4$  years,  $^{240}\text{Pu}$  has a half-life of  $6.57 \times 10^3$  years, and the  $^{242}\text{Pu}$  isotope, which was used as a yield tracer, has a half-life of  $3.76 \times 10^5$  years. Due to their relatively longer half-lives, decay correction of these isotopes was not needed. The energy levels of alpha particles of  $^{242}\text{Pu}$  are 4.90 MeV (74 %) and 4.86 MeV (26 %). The alpha energy levels of  $^{239}\text{Pu}$  are 5.16 MeV (73.3 %), 5.15 MeV (15.1 %), and 5.10 MeV (11.5%) and those of  $^{240}\text{Pu}$  are 5.16 MeV (75.5 %), 5.12 MeV (24.4 %) and 5.01 MeV (0.091 %). Due to the similar alpha energies of the  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  peaks, they are inseparable by an alpha counter. Therefore, the activities of both isotopes are measured together and always written as  $^{239,240}\text{Pu}$ . Since the activities of Pu isotopes are relatively low in the sediments, the background counts in the alpha counter are closely monitored and subtracted from the gross counts. The activity of  $^{239,240}\text{Pu}$  is calculated as:



$$^{239,240}\text{Pu activity (dpm/kg)} = \frac{^{239,240}\text{Pu counts (net)}}{^{242}\text{Pu counts (net)}} \times \frac{^{242}\text{Pu Activity (dpm)}}{\text{Sample weight (g)}} \times 1000$$

The yield tracer solutions of  $^{208}\text{Po}$ , and  $^{242}\text{Pu}$  were obtained from the Environmental Measurements Laboratory (courtesy of Dr. Bob Anderson, Lamont Doherty Earth Observatory, NY). They were previously calibrated against standards which are traceable to NBS standards.

The errors associated with the alpha counting method can be calculated as below. If X represents the number of net counts from the isotope of interest, Y represents the number of net counts from the spike isotope, and x and y are the errors of X and Y, respectively, then the propagated error (1 sigma) associated with the counting is:

$(X / Y) \pm (X/Y) * [(x/X)^2 + (y/Y)^2]^{1/2}$  where, x is the square root of X and y is the square root of Y.

#### 4) Gamma counting procedures

The list of isotopes to be analyzed is given in Table 1.

**TABLE 1. LIST OF ISOTOPES**

| Isotope           | Half life  | Gamma<br>Energy (keV) |
|-------------------|------------|-----------------------|
| <sup>210</sup> Pb | 22 years   | 46                    |
| <sup>234</sup> Th | 24 days    | 63                    |
| <sup>226</sup> Ra | 1600 years | 352                   |
| <sup>228</sup> Ra | 5.7 years  | 338,911               |
| <sup>7</sup> Be   | 53 days    | 478                   |
| <sup>137</sup> Cs | 30 years   | 662                   |

#### 4.1) <sup>226</sup>Ra (352 keV) and <sup>210</sup>Pb (46 keV)

The <sup>226</sup>Ra activities in dry sediment samples are determined by a non destructive gamma counting method. Each section is measured for <sup>226</sup>Ra, via its grand-daughter <sup>214</sup>Pb, at a photopeak of 352 keV. The gamma counting instrument used has a well-type germanium detector, which consists of a pure germanium closed-end coaxial well crystal of 36 mm depth and 20 mm diameter. The crystal has an active volume of 140.5 cm<sup>3</sup>. The resolution of the detector is 1.54 keV for <sup>57</sup>Co (122 keV photo peak) and 2.24 keV for <sup>60</sup>Co (1332 keV photo peak). The gamma counting system, including the multi-channel analyzer, was previously calibrated with liquid and sediment standards containing <sup>210</sup>Pb, <sup>234</sup>Th, <sup>226</sup>Ra and <sup>228</sup>Ra isotopes for various geometries (BASKARAN et al., 1993a). As the geometry increases from 1 ml to 10 ml, the counting efficiency varies almost by a factor of 2.5. There is no background peak observed for <sup>226</sup>Ra. The activity of <sup>226</sup>Ra in the sediment samples is calculated using the formula:

$$^{226}\text{Ra (dpm/g)} = \frac{^{226}\text{Ra Net counts}}{\text{Counting time (min)}} \times \frac{\text{DPM/CPM conversion factor}}{\text{Sample weight (g)}}$$

The counting uncertainty (1 standard deviation) was previously determined as 4-8 % for sediment samples, and the final one-sigma-propagated-error (errors from: 1σ counting error, error due to the background correction, and error from separately conducted calibrations) was always less than 10%. Repeated measurements of the fly-ash sediment standard over long periods of time showed that the stability of the counting system was better than 10%.

#### *Analysis of standard reference material for <sup>210</sup>Pb and <sup>226</sup>Ra*

To ensure that the alpha and gamma counting instruments were well calibrated, and that the microwave digestion method extracted all of the <sup>210</sup>Pb in the sediment samples, a Fly Ash sediment standard (a by-product of coal combustion), from the National Bureau of Standards, was measured for Pb-210 and Ra-226. About 1 g of Fly Ash sediment standard was taken in a microwave digestion vessel, digested for Pb-210, plated, and alpha counted.

Also, about 5 ml (5.85 g) of the same sediment was taken in a counting vial, and gamma counted for Ra-226. The results indicated that the measured  $^{210}\text{Pb}$  activity in this sediment standard was  $7.86 \pm 0.41$  dpm/g while the  $^{226}\text{Ra}$  activity was  $7.71 \pm 0.35$  dpm/g. These values are, within the errors, the same as that of the NBS certified  $^{226}\text{Ra}$  activity of  $7.80 \pm 0.51$  dpm/g. These results confirm the analytical capability of the alpha and gamma counting instruments, as well as the 100% yield of the microwave digestion technique for  $^{210}\text{Pb}$ . Selfadsorption corrections for  $^{210}\text{Pb}$  are, however, applied when needed for samples with packing densities in the vial significantly different than  $1 \text{ g cm}^{-3}$ .

#### 4.2) $^{234}\text{Th}$ (63 keV).

Standard reference materials used for geometry calibrations were previously obtained from standards obtained by US-EPA-EMSL, as well as liquid standards of  $^{238}\text{U}$ . Selfadsorption corrections are applied when needed for samples with packing densities in the vial significantly different than  $1 \text{ g cm}^{-3}$ . All reported results of [ $^{234}\text{Th}$  -  $^{238}\text{U}$ ] are decay corrected to the time of sample collection, with  $^{238}\text{U}$  activities taken where  $^{234}\text{Th}$  activities remain constant (secular equilibrium) which occurs deeper in the core.

#### 4.3) $^{137}\text{Cs}$ (662 keV).

Standard reference materials used for geometry calibrations were previously obtained from New England Nuclear Corporation, Dreieich, Germany.

#### 4.4) $^7\text{Be}$ (478 keV).

Standard reference materials used for geometry calibrations were obtained from Laboratoire de Meteorologie des Rayonnements Ionisants, Gif-sur-Ivette, France..

#### 4.5) Reporting of Activity Concentrations

Activities are reported as dpm/kg or Bq/kg.  $60 \text{ dpm} = 1 \text{ Bq} = \text{dps}$ .

#### 4.6) Hazards and Precautions

Even though the radionuclides analyzed pose no health hazard, all heating and chemical processing of the sediment samples will be carried out in a hood. Have material safety data sheets and first aid kits on hand. Disposal of any solutions and sediments will follow the University's Health and Safety Regulations.

## APPENDIX II

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